5

PROCESS FOR THE SELECTIVE CATALYTIC HYDRODEALKYLATION OF ALKYLAROMATIC HYDROCARBONS

The present invention relates to a process for the

10   catalytic hydrodealkylation of alkylaromatic hydrocarbons.

More specifically, the present invention relates to a process for the catalytic hydrodealkylation of hydrocarbon compositions comprising C_8-C_{13} alkylaromatic compounds, optionally in a mixture with C_4-C_9 aliphatic and

15   cycloaliphatic products.

Even more specifically, the present invention relates to a process for the catalytic hydrodealkylation of alkylaromatic hydrocarbons, in a mixture with aliphatic products, wherein the reaction takes place in the presence

20   of water. The presence of water, together with the choice of suitable operative conditions and catalyst formulation, make the reaction, object of the invention, surprisingly selective towards the hydrodealkylation of alkylaromatic products, and efficient in quantitatively suppress-

25   ing transalkylation, isomerization, disproportioning and

condensation side-reactions.

This leads to a high yield in benzene, toluene and ethane (BTE) and reduced or non-formation of both methane and condensed products, essentially naphthalene and biphenyl products.

Processes for the catalytic conversion of alkylaromatic products are known in literature, wherein the addition of water under the process conditions, specifically promotes isomerization, disproportioning and transalkylation reactions, significantly jeopardizing the hydrodealkylation reaction, thus obtaining opposite results to those object of the present invention.

U.S. patent 4,431,857, for example, describes a catalytic process, carried out in the presence of a crystalline boron-silicate catalyst (AMS-1B) impregnated with molybdenum, wherein the addition of water, from 50 to 2000 ppm, to the feeding mix consisting of xylenes (ortho- meta- and para-) and ethylbenzene, causes their isomerization to para-xylene, thus inhibiting the direct dealkylation.

U.S. patent 5,773,679, describes a process for the catalytic conversion selectively directed towards the disproportioning reaction of toluene to para-xylene by the addition of water, in continuous or intermittently (from 0.01 to 10 ml*g/min), to the feeding mix, using a ZSM-5 zeolite treated with a silanizing agent. The ethylbenzene, ini-

tially present, and the heavier alkylaromatic products which are formed, however, do not undergo dealkylation under the reaction conditions.

U.S. patent 6,512,155 describes a sole isomerization
5   process carried out in the presence of water (from 75 to 750 ppm) in order to bring mixtures of xylenes, under non-equilibrium conditions, together with ethylbenzene, towards the selective production of p-xylene, so as to have a final equilibrium composition of xylenes. The reaction proceeds
10   in the presence of a zeolitic or non-zeolitic catalyst impregnated with Pt, and water is added in continuous or intermittently, as such or by means of an organic precursor (alcohol, ester, ether) capable of supplying it under the reaction conditions.

15   U.S. patent 6,500,997 describes a process for the conversion of C_7-C_{10} alkylaromatic products via disproportioning/transalkylation, to obtain mainly xylenes, with an equilibrium composition, carried out on a catalyst based on mordenite or β-zeolite impregnated with bismuth. In this
20   case, the presence of water in the reaction is undesired, but the system guarantees, according to the invention, the maintenance of a high stability and activity even when water is present up to 500 ppm.

As far as the operative conditions and choice of cata-
25   lyst are concerned, European patent 138,617 describes a

process for the conversion of aromatic hydrocarbons by means of hydrodealkylation which comprises the treatment of a hydrocarbon stream, essentially consisting of ethylbenzene and xylenes, under conventional reaction con-

5   ditions, with a zeolite catalyst modified with molybdenum. In the process described, the general reaction conditions do not allow a hydrodealkylation reaction without contemporaneous isomerization, transalkylation, disproportioning and condensation reactions. The limitations towards a se-

10   lective catalytic hydrodealkylation also emerge from various other processes described in the known art. In some cases, this reaction even forms a side-reaction with respect to the isomerization, transalkylation, disproportioning and condensation reactions.

15   The Applicant has now unexpectedly found that it is possible to induce the-catalytic hydrodealkylation reaction alone, in the presence of water, of C_8-C_{13} alkylaromatic hydrocarbons to benzene, toluene and ethane (BTE), without contemporaneous isomerization, transalkylation, dispropor-

20   tioning and condensation reactions, by selecting suitable operative conditions and catalyst formulation.

         In particular, the presence of water and the catalyst composition, both object of the present invention, have surprisingly allowed the selection of operative conditions

25   so   as   to   favour   the   hydrodealkylation   alone   of

alkylaromatic compounds. According to the process, object of the invention, not only is the hydrodealkylation reaction quantitatively selective towards the formation of benzene, toluene and ethane, with a reduced or null production

5   of methane and condensed products (naphthalene and biphenyl derivatives), but the benzene/toluene ratio is always decidedly favorable towards benzene. The economical aspect of the process can therefore be referred to the intrinsic value of both the reaction streams: the liquid phase due to

10   the remunerative value of benzene and toluene, with particular reference to benzene, always produced in larger quantities than toluene; the gaseous phase as a result of the possibility of recycling the ethane produced to any pyrolysis process, for example by recycling to ovens, with

15   the considerable energy recovery guaranteed by this type of recycling.

An object of the present invention therefore relates to a process for the catalytic hydrodealkylation alone of hydrocarbon compositions comprising C_8-C_{13} alkylaromatic

20   compounds, possibly mixed with C_4-C_9 aliphatic and cycloaliphatic products, which comprises the treatment, in continuous, in the presence of water, of said hydrocarbon compositions with a catalyst consisting of a ZSM-5 zeolite carrier having a molar ratio Si/Al of between 5 and 35,

25   modified with at least one metal selected from those be-

longing to groups IIb, VIB and VIII, at a temperature rang-
ing from 400 to 700°C, preferably between 450 and 600°C, a
pressure ranging from 2 to 4 MPa, preferably between 2.8
and 3.6 MPa, a molar ratio between water and hydrocarbon

5   charge ranging from 0.0006 to 0.16 (i.e. between 0.01 and
2.5% w/w), more preferably between 0.003 and 0.032 (i.e.
between 0.05 and 0.5% w/w), a molar ratio H_2/charge of be-
tween 3 and 6, preferably between 3.8 and 5.2.

According to the present invention, the hydrocarbon

10   charge which undergoes hydrodealkylation comprises C_8-C_{13}
alkylaromatic compounds, such as ethylbenzene, xylene,
diethylbenzenes,   ethylxylenes,   trimethylbenzenes,
tetramethylbenzenes,   propylbenzenes,   ethyltoluenes,
propyltoluenes etc.. This charge can come, for example,

15   from effluents of reforming units or units which effect py-
rolytic processes, such as steam cracking, and can possibly
contain a mix of C_4-C_9 aliphatic and cycloaliphatic prod-
ucts and organic compounds containing heteroatoms, such as,
for example, sulfur, in the typical amounts generally pre-

20   sent in charges deriving from reforming units or pyrolysis
processes.

The hydrocarbon charge used in the present process can
also be subjected to separation treatment, for example dis-
tillation or extraction, to concentrate the products which

25   must subsequently undergo hydrodealkylation, or it can be

treated with aromatization processes to increase the con-
centration of alkylaromatic compounds and decrease the par-
affin concentration. Furthermore, a previous hy-
drogenation of the charge may also be necessary, to elimi-

5   nate the unsaturations present in the aliphatic compounds
and on the same alkyl substituents of the aromatic rings.
The same hydrogenation can remove sulfur, nitrogen or oxy-
gen from the substances typically present in the charge to
be treated, even if this latter aspect is not of particular

10   importance as, under the catalytic hydrodealkylation
conditions, according to the present invention, these het-
eroatoms are quantitatively removed (sulfur, for example,
as H_2S).

The hydrodealkylation catalyst, according to the pre-

15   sent invention, consists of a ZSM-5 zeolite modified with
at least one metal selected from those of groups IIB, VIB
and VIII. Molybdenum is preferred among the metals, object
of the invention, used either singly or in pairs. The com-
position of the zeolite carrier is particularly important

20   for the embodiment of the present invention, which com-
prises the hydrodealkylation of alkylaromatic compounds
with the substantial absence of isomerization,
transalkylation, disproportioning and condensation side-
reactions. It has been verified that the use of a ZSM-5

25   zeolite with a high aluminum content, in particular having

Si/Al molar ratios of between 5 and 35, preferably between 15 and 30, contributes to obtaining the desired result.

ZSM-5 zeolites are available on the market or can be prepared according to the methods described in U.S. patents

5   3,702,886 and 4,139,600. The structure of ZSM-5 zeolites is described by Kokotailo et al. (Nature, Vol. 272, page 437, 1978) and by Koningsveld et al. (Acta Cryst. Vol. B43, page 127, 1987; Zeolites, vol. 10, page 235, 1990).

In the process of the present invention, the zeolite

10 catalyst is preferably used in bound form, adopting a bind-ing compound capable giving it form and consistency, for example mechanical resistance, so that the zeolite cata-lyst/binder can be conveniently used in an industrial re-actor. Examples of binders include aluminas, among which

15 pseudo-bohemite and γ-alumina; clays, among which kaolin-ite, vermiculite, attapulgite, smectites, montmorillonites; silica; alumino-silicates; titanium and zirconium oxides; combinations of two or more thereof, used such quantities as to have zeolite/binder weight ratios ranging from 100/1

20 to 1/10.

The dispersion of metals in the zeolite or zeo-lite/binder catalyst can be carried out according to con-ventional techniques, such as impregnation, ion exchange, vapor deposition, or surface adsorption. The incipient im-

25 pregnation technique is preferably used, with an aqueous or

aqueous-organic solution (the organic solvent being pref-
erably selected from alcohols, ketones and nitriles or mix-
tures thereof), containing at least one hydro- and/or or-
gano-soluble of the metal, with a final total content of
5   the metal in the catalyst ranging from 0.5 to 10% by
weight.

The zeolite, with or without a binder, is subjected to
impregnation with a metal of groups IIB, VIB and VIII, in
particular, molybdenum.

10   The bound or non-bound catalyst can be treated accord-
ing to methods which include:

-     preparing one or more solutions of compounds of the
metals to be carried;

-     impregnating the zeolite with the above solutions;

15   -   drying the zeolite thus impregnated:

-     calcining the zeolite, impregnated and dried, at tem-
peratures of between 400 and 650°C;

possibly repeating the above steps several times, according
to necessity.

20   Examples of compounds of the metals used are: molybde-
num(II) acetate, ammonium(VI) molybdate, diammonium(III)
dimolybdate, ammonium(VI) heptamolybdate, ammonium(VI)
phosphomolybdate and analogous salts of sodium and potas-
sium, molybdenum(III) bromide, molybdenum(III)-(V) chlo-
25   ride, molybdenum(VI) fluoride, molybdenum(VI) oxychloride,

molybdenum(IV)-(VI) sulfide, molybdic acid and the corre-
sponding acidic salts of ammonium, sodium and potassium,
and molybdenum(II-VI) oxides.

5   At the end of the impregnation, the total metal con-
tent, alone or in pairs, in the catalyst ranges from 0.1 to
10% by weight, preferably from 0.5 to 8% by weight.

Once the preparation of the catalyst has been com-
pleted, the same is charged into a fixed-bed reactor, fed
in continuous with the hydrocarbon charge, hydrogen and wa-
10   ter. The water is fed, according to convenience, either al-
ready vaporized, so that it can be mixed directly with the
hydrocarbon charge, previously brought to gas phase, or by
the addition of a carrier compound, miscible with the liq-
uid charge, capable of releasing it under the reaction con-
15   ditions.

Among compounds miscible with the liquid hydrocarbon
charge, alcohols, ethers and esters can be used. Alcohols
are preferred, and among these ethanol or phenethyl alco-
hol. For example, ethyl alcohol releases the water desired
20   and ethylene, under the reaction conditions. The latter is
immediately hydrogenated to ethane, adding it to the amount
present   in   the   gas   phase selectively produced by
the hydrodealkylation reaction.

Among the fundamental experimental parameters, the se-
25   lection of the flow rate of the reagents is of vital impor-

tance in order to obtain a selective hydrodealkylation of the C_8-C_{13} aromatic hydrocarbons possibly in a mixture with C_4-C_9 aliphatic and cycloaliphatic hydrocarbons. The feeding rates of the hydrocarbon, water and hydrogen mix, or of

5   the carrier compound, must therefore be such as to guarantee an LSHV (Liquid Hourly Space Velocity), calculated on the hydrocarbon stream, ranging from 3 to 5 h^{-1} and, more preferably, between 3.5 and 4.5 h^{-1}.

For this purpose, the molar ratio between hydrogen and

10   the charge fed to the reactor must remain within the range of 3 to 6 mol/mol, more preferably between 3.8 and 5.2 mol/mol. In particular, the molar ratio between the water and hydrocarbon charge fed to the reactor is between 0.0006 and 0.16 (i.e. between 0.01 and 2.5% w/w), more preferably

15   between 0.003 and 0.032 (i.e. between 0.05 and 0.5% w/w).

The experimental apparatus for the reaction includes a stainless steel fixed-bed reactor with an internal diameter of 20 mm and a total height of 84.5 cm, an electric heating device surrounding the reactor, a cooling system, a gas-

20   liquid separator and a liquid high pressure pump.

The isothermal section of the reactor, maintained at a constant temperature by automatic control, is charged with the catalyst. The remaining reactor volume is filled with an inert solid in granules, for example, corundum, in order

25   to guarantee an optimal distribution and mixing of the

gaseous reagent flow before the catalytic bed and the heat supplied to the reaction.

A pre-heater, positioned before the reactor, which operates at a temperature ranging from 200 to 400°C, more

5   preferably between 250 and 320°C, contributes to the optimal contact of the reagents in gaseous phase (hydrocarbon mix, water and hydrogen) with the catalyst. This system favours the establishment of isothermal conditions in very rapid times, not only limited to the fixed-bed, but also

10   along the whole reactor, allowing an easier and more accurate control of the operating temperature of the catalyst. The liquid and gaseous effluents produced by the reaction are separated and analyzed via gas chromatography, at intervals.

15   The following examples provide a further illustration of—the process according to the present —invention and should in no way be interpreted as limiting its scope as indicated in the enclosed claims.

REFERENCE EXAMPLE FOR THE CATALYST PREPARATION

20   Catalyst A   (comparison)

A catalyst A is prepared, obtained by mixing a ZSM-5 zeolite and an alumina as binder, the two phases being in a weight ratio of 60/40, and extruding the mixture.

The extruded product is calcined in air at 550°C for 5

25   hours and its surface area BET is 290 m^2/g.

Once at room temperature, the above is crushed and sieved to produce a powder having dimensions of between 20 and 40 mesh (between 0.84 mm and 0.42 mm), so that 12.4 g of catalyst powder have an equivalent volume of 20 ml.

5   Catalyst B

Catalyst B is obtained by impregnating catalyst A (50 g) with an aqueous solution (60 ml) containing 1.88 g of ammonium molybdate $[(NH_4)_6Mo_7O_{24} \bullet 4H_2O]$ at about 25°C for 16 hours, and is subsequently placed under a nitrogen flow for

10 12 hours, dried in an oven at 120°C for 4 hours under vacuum and calcined in air at 550°C for 5 hours. The calculated molybdenum content is 2.0% by weight, against the value of 2.1% by weight determined by means of ICP-MS analysis.

15 EXAMPLES 1-9

The reactor is charged with 20 cm^3 (12.4 g) of catalyst A, whereas the remaining volume is filled with granules of corundum to guarantee the optimal distribution and mixing of the gaseous flow of the reagents and of the heat

20 supplied to the reaction.

The hydrocarbon charges, whose compositions are indicated in Table 1, are fed to the reactor suitably mixed with hydrogen. The aliphatic fraction in the charge consists of C_4-C_9 products and the saturated C_5 indane ring.

25 The ethanol present in Charge 2 in an amount of 5% w/w sup-

plies a quantity of equivalent water of 1.95% w/w.

Table 1 – Composition of the feeding charge

Charge type	Charge 1	Charge 2
Concentration	weight %	weight %
Ethanol (H_2O as carrier)	--	5
Ethylbenzene	34	32.3
o, m, p-xylene	32	30.4
Indane	9	8.6
Cumene	1	0.9
n-propylbenzene	3	2.9
2-, 3-, 4-ethyltoluene	16	15.2
Σ (C_4-C_9 Aliph. + C_{9+} Arom.)	5	4.7
Total	100	100

The reaction is carried out at a pressure of 3 MPa with a flow-rate of the reagent charge which is such as to have an LHSV of 3.9-4.1 h^{-1}, and a molar ratio H_2/charge of 4.2-4.4. The results are indicated in the following table 2.

Table 2

Example	1	2	3	4	5	6	7	8
Reaction temperature	510 °C	510 °C	510 °C	510 °C	550 °C	550 °C	550 °C	550 °C
Catalyst	A	A	B	B	A	A	B	B
Charge	1	2	1	2	1	2	1	2
Charge conversion (%)	78.6	76.4	84.5	80.9	81.3	76.1	88.7	81.8
Liquid effluent composition	weight %	weight %	weight %	weight %	weight %	weight %	weight %	weight %
Methane	10.3	2.6	3.2	1.0	13.8	2.7	7.0	1.5
Ethane (E)	11.2	6.8	20.6	14.8	11.4	9.7	19.2	15.4
Σ C3	3.1	7.8	3.8	3.3	1.3	7.5	2.2	2.5
Σ C4-C5	...	0.2	0.1	0.1	...	0.2	0.1	0.1
Ethyl benzene	0.9	2.8	0.2	1.0	0.8	3.5	0.1	0.6
o, m, p-xylene	15.9	20.2	13.1	16.4	14.5	21.3	10.0	15.5
Indane	...	...	...	...	...	...	...	...
Cumene	...	...	...	...	...	...	...	...
Σ C9-C9+ Aromatic compounds	5.5	4.2	3.0	3.3	5.0	2.4	1.9	2.4
Benzene (B)	24.0	29.2	27.2	33.8	26.3	26.9	29.6	35.1
Toluene (T)	28.4	26.2	28.8	26.3	26.9	25.8	29.9	26.9
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Σ BT	52.4	55.4	56.0	60.1	53.3	52.7	59.5	62.0
Selectivity to BT	66.7	72.5	66.3	74.3	65.6	69.3	67.1	75.8
Σ BTE	63.9	62.2	76.6	74.9	64.7	62.4	78.7	77.4
Selectivity to BTE	80.9	81.4	90.6	92.6	79.6	82.0	88.7	94.6
R(B/T)	0.76	1.12	0.94	1.29	0.98	1.04	0.99	1.31
R(BE/T)	1.24	1.37	1.66	1.85	1.40	1.42	1.63	1.88

Table 3

Example	4	8	9
Reaction temperature	510 °C	550 °C	585 °C
Catalyst	B	B	B
Charge	2	2	2
Charge conversion (%)	80.9	81.8	86.1
Liquid effluent composition	weight %	weight %	weight %
Methane	1.0	1.5	1.6
Ethane (E)	14.8	15.4	16.1
Σ C3	3.3	2.5	1.8
Σ C4-C5	0.1	0.1	0.1
Ethyl benzene	1.0	0.6	0.4
o, m, p-xylene	16.4	15.5	11.3
Indane	...	...	...
Cumene	...	...	...
Σ C9-C9+ Aromatic compounds	3.3	2.4	1.8
Benzene (B)	33.8	35.1	37.5
Toluene (T)	26.3	26.9	29.0
Total	100.0	100.0	100.0
Σ BT	60.1	62.0	66.5
Selectivity to BT	74.3	75.8	77.2
Σ BTE	74.9	77.4	82.6
Selectivity to BTE	92.6	94.6	95.9
R(B/T)	1.29	1.31	1.29
R(BE/T)	1.85	1.88	1.85

Under the same operating conditions, it can be ob-
served (see Table 2, Examples 1-8) how, both at 510 and
550°C, the selectivity of the hydrodealkylation reaction to
Benzene plus Toluene (BT, liquid phase) or to Benzene plus
5   Toluene plus Ethane (BTE, liquid phase and gas phase) is
always the highest when the ZSM-5/Mo catalytic system is
operating in the presence of H_2O (Examples 4 and 8).

The B/T and BE/T ratios which can be considered as
"main indexes" of the hydrodealkylation selectivity, give
10   an immediate vision of this positive trend.

Table 3 (Examples 4, 5 and 9) and Figure 1 enclosed,
show how, under the same overall operating conditions, the
temperature rise to 585°C (Example 9) allows the conversion
of the charge to be increased to values typical of tests
15   with molybdenum alone. This conversion recovery is obtained
as a result of a significant reduction in the residual con-
centration of xylenes and heavier aromatics (C_9-C_{9+}). The
quantity of xylenes and higher aromatic products converted
per single passage is such as to sustain their recycling to
20   the reactor affluent.

The concentration of methane deriving from the
hydrgenolysis of the aromatic ring (generally favoured at
the highest temperatures), does not change significantly
and in the tests with H_2O, it always remains substantially
25   lower than that obtained with molybdenum alone. Further-

more, the contemporaneous reduction in heavier aromatic products (C_9-C_{9+}) minimizes the possibility of the formation of condensation side-reactions (also generally favoured at the highest temperatures) which create polycondensed aro-

5   matic products and coke which deactivate the catalyst.

All these results indicate the unexpected existence of an extremely strong synergy between the catalyst and H_2O to the extent that the overall ZSM-5/Mo/H_2O system should be considered as being the real reaction catalyst. The results

10   relating to the conversion and selectivity and consequently also to the activity, indicate a surprising stability of the catalytic system with respect to degradation effects due to the presence of water also at high temperatures, unlike what is described in the known art.

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